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Angélil, Raymond ; Diemand, Jürg ; Tanaka, Kyoko K ; Tanaka, Hidekazu

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DOI: https://doi.org/10.1063/1.4803195

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Citation: AIP Conference Proceedings **1527**, 23 (2013); doi: 10.1063/1.4803195
View online: http://dx.doi.org/10.1063/1.4803195
View Table of Contents: http://scitation.aip.org/content/aip/proceeding/aipcp/1527?ver=pdfcov
Published by the AIP Publishing

The Physics of Nucleated Droplets in Large-Scale MD Lennard-Jones Simulations

Raymond Angélil[a], Jürg Diemand[a], Kyoko K. Tanaka[b] and Hidekazu Tanaka[b]

[a]*Institute for Theoretical Physics, University of Zürich, 8057 Zurich, Switzerland*
[b]*Institute of Low Temperature Science, Hokkaido University, Sapporo 060-0819, Japan*

Abstract. We have performed large-scale Lennard-Jones molecular dynamics simulations of homogeneous vapor-to-liquid nucleation, typically with $N \sim (1-8) \times 10^9$. Our work continues on from [4, 5], except at lower vapor densities. The large size of these simulations is primarily necessitated by the rarity of nucleation events at these low supersaturations. A further benefit gained from large simulations is the substantial number of nucleated droplets which are able to continue growing without significantly dropping the vapor density. This allows us to study the properties of clusters as they grow, embedded within an unchanging external environment. This is particularly important in understanding the role that the droplet's surface plays in the development of the droplet - as a bustling interface between the denser (and ever-growing) core, and the stable vapor outside. The nucleation properties of the vapor as a whole are presented in a separate contribution (Diemand et al.), while here we explore the properties of the clusters themselves, once formed.

Keywords: drops, equations of state, Lennard-Jones potential, molecular dynamics method, nucleation, solid-vapour transformations
PACS: 05.10.-a, 05.70.Fh, 05.70.Ln, 05.70.Np, 36.40.Ei, 64.60.qe, 64.70.Hz, 64.60.Kw, 64.10.+h, 83.10.Mj, 83.10.Rs, 83.10.Tv

THE SIMULATION

The simulation we analyse here, designated *T6n8*, is part of a larger suite of runs (Diemand et al. in these proceedings), all performed with the Large-scale Atomic/Molecular Massively Parallel Simulator [2], primarily on the Hermit Cray XE6 supercomputer in Stuttgart. This run contains a billion atoms with random initial conditions in a cube with periodic boundary conditions. Figure. 1 shows snapshots taken at the end of the simulation.

The potential is Lennard-Jones, truncated at 5σ, where σ is the Lennard-Jones potential zero-point. This potential is especially applicable for noble gases, like argon. The initial density of this simulation is $8 \cdot 10^{-3}\sigma^{-3}$. 500'000 timesteps were performed, or in Lennard-Jones time units, $t_{\text{end}} = 5'000\tau$. The temperature of the system is $T = 0.6\varepsilon/k$. Were this gas argon, our simulation would run for $t_{\text{end}} = 10.8$ns, at temperature $T = 72$K in a box with edges of length 1.7μm. Groups are identified by a friends-of-friends algorithm. The critical size of the droplets as predicted by the semi-phenomenological nucleation model is $i^* = 16$. A few thousand post-critical clusters are produced over the entire run. These clusters quickly grow, and by the end of the run, the largest cluster has > 200 atoms. The nucleation rate is estimated in Figure. 2. The largest cluster's size evolution is also shown in this figure, from which the sticking probability can be

Nucleation and Atmospheric Aerosols
AIP Conf. Proc. 1527, 23-26 (2013); doi: 10.1063/1.4803195

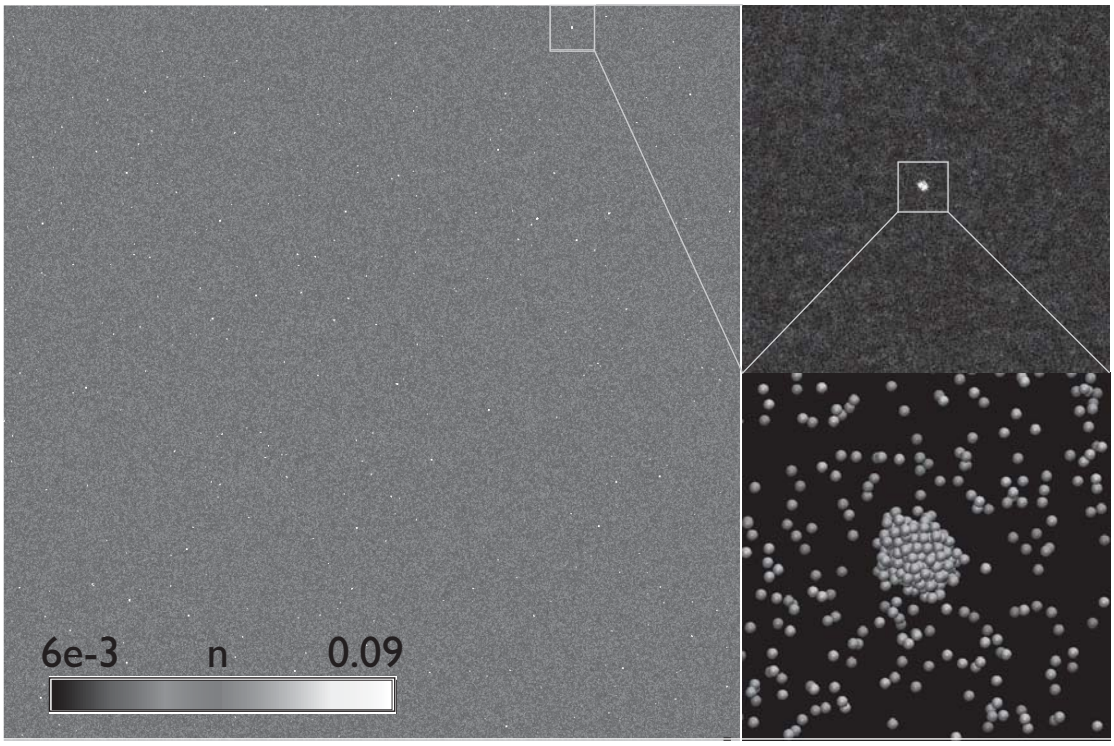
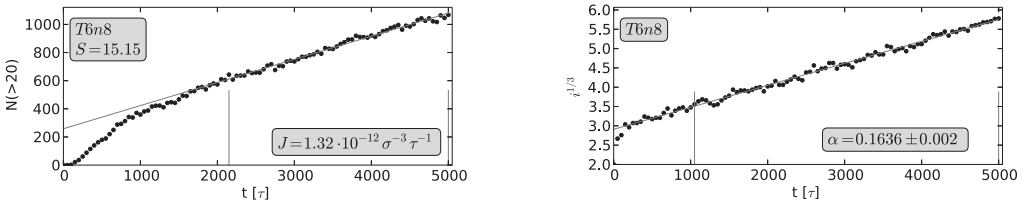


FIGURE 1. A snapshot taken at the end of the simulation. The left panel shows the entire box, $5000\sigma \times 5000\sigma$, with a depth of 300σ. The insert in the upper-right is $300\sigma \times 300\sigma \times 300\sigma$. The final insert in the bottom right is $40\sigma \times 40\sigma \times 20\sigma$. The cluster in view here has 220 members.



(a) (b)

FIGURE 2. Panel (a) shows the number of clusters in the simulation with a size greater than 20. From this slope, once the lag phase is over, the nucleation rate can be calculated. Panel (b) shows the growth of the largest cluster, from which the sticking probability α can be estimated.

estimated.

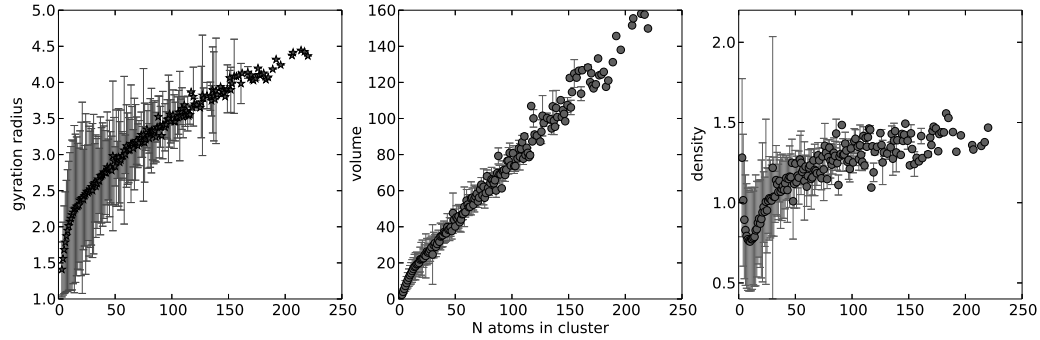
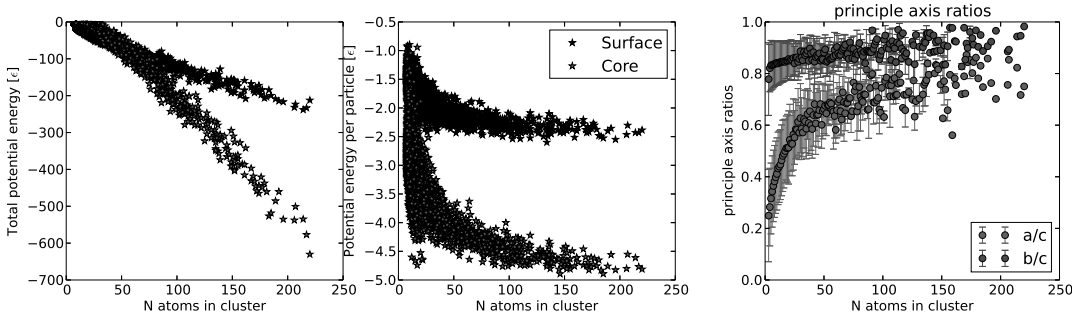


FIGURE 3. Distributions of size, volume, and density of the clusters at the end of the run. Note the kink in the volume that occurs around clusters of size 20. Once the clusters are large enough to support cores (atoms with at least 7 neighbours by our definition), the average volume drops.



(a) (b)

FIGURE 4. Panel (a) plots the potential energies of the particles in clusters. Panel (b) shows the ellipticity of the clusters, as determined by principle component analysis. The clusters become more spherical as they grow, yet remain significantly ellipsoidal at all sizes.

CLUSTER PROPERTIES

Figure. 3 shows the sizes of the clusters - in this case, the gyration radius (the average root mean square atom distance from the center of gravity) - as a function of the number of atoms in the cluster. From this, the volume and density of the clusters can be calculated. A curious kink is visible around $i \sim 20$, indicating a decrease in the average volume as soon as the cluster is large enough to bear a significant number of core atoms. Figure. 4 plots the spread in potential energies of the atoms against cluster atom count. A 'core' particle is defined as one which has at least 7 neighbours within the search radius ($r_c = 1.41$). The potential energies per particle for both populations of atoms - core and surface, continues decreasing as the cluster sizes increase. These findings likely will play an important role in understanding the dynamics of the clusters, including their growth rates. These results are at odds with the standard picture of constant-density liquid droplets. Theoretical aspects of the core-surface framework have been explored in [1]. A detailed analysis of the cluster surface energies will shed light on various aspects

of the nucleation process by helping estimates for the free energy of formation, and so aid further model-building.

Principal component analysis gives us the cluster ellipticity distribution, shown in Figure. 4. Although the clusters become more spherical as they grow, they are still significantly elliptical at all sizes - in contrast to the standard model assumption that nucleated liquid droplets are spherical. Formation energy models tackling the issue of non-sphericity in clusters has been addressed in [3].

ACKNOWLEDGMENTS

We acknowlede a PRACE award (36 million CPU hours) on Hermit at HLRS. Additional computations were preformed on SuperMUC at LRZ, on Rosa at CSCS and on the zBox4 at UZH. J.D. and R.A. are supported by the Swiss National Science Foundation.

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